



Freezing-enhanced reduction of chromate by nitrite



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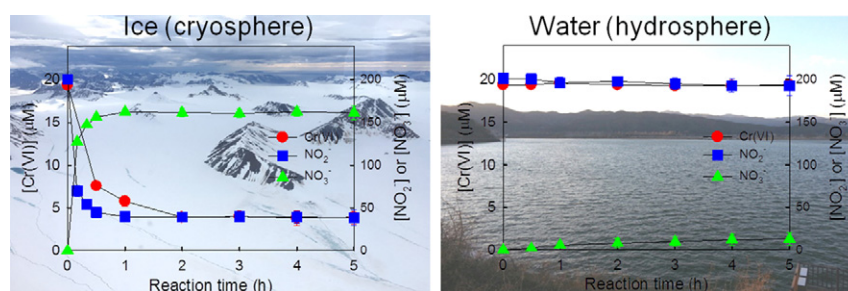
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HIGHLIGHTS

- Reduction of Cr(VI) by NO_2^- was significantly enhanced during freezing.
- NO_2^- was primarily oxidized to NO_3^- in ice.
- Enhanced Cr(VI) reduction in ice is ascribed to the freeze concentration effect.
- Reduction of Cr(VI) was enhanced by freezing under various conditions.
- Freezing-enhanced reduction of Cr(VI) in the electroplating wastewater was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

The redox reactions between pollutants and chemicals (e.g., pollutant, oxygen, and water) critically affect the fate and potential risk of pollutants, and their rates significantly depend on the environmental media. Although the kinetics and mechanism of various redox reactions in water have been extensively investigated, those in ice have been hardly explored, despite the large areal extent of the cryosphere, which includes permafrost, polar regions, and mid-latitudes during the winter season on Earth. In this study, we investigated the reduction of chromate (Cr(VI)) by nitrite (NO_2^-) in ice (i.e., at $-20\text{ }^\circ\text{C}$) in comparison with its counterpart in water (i.e., at $25\text{ }^\circ\text{C}$). The reduction of Cr(VI) by NO_2^- was limited in water, whereas it was significant in ice with the simultaneous oxidation of NO_2^- to nitrate (NO_3^-). This enhanced Cr(VI) reduction by NO_2^- in ice is most likely due to the freeze concentration effect, that concentrates Cr(VI), NO_2^- , and protons (at acidic conditions) in the liquid brine (the liquid region among solid ice crystals). The increased thermodynamic driving force for the redox reaction between Cr(VI) and NO_2^- by the freeze concentration effect (i.e., the increase in concentrations) enhances the reduction of Cr(VI) by NO_2^- . The freezing-enhanced Cr(VI) reduction by NO_2^- was observed under the conditions of NO_2^- concentration = $20\text{ }\mu\text{M}$ – 2 mM and $\text{pH} = 2$ – 4 , which are often found in real aquatic systems contaminated by both Cr(VI) and NO_2^- . The reduction kinetics of Cr(VI) in real Cr(VI)-contaminated wastewater (electroplating wastewater) during freezing was significant and comparable to that in the artificial Cr(VI) solution. This result implies that the proposed ice/Cr(VI)/ NO_2^- process should be relevant and feasible in real cold environments.

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1. Introduction

Chemical reactions in ice (i.e., at temperatures below the freezing point) are different from those in water (i.e., at temperatures above the freezing point). A liquid region remains among the solid ice crystals

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and on the ice crystal surface at temperatures below the freezing point, although its volume continuously decreases with the growth of ice crystals with time (Bartels-Rausch et al., 2014; Boxe and Saiz-Lopez, 2008; Park et al., 2010). This liquid region in ice is often referred to as liquid brine, liquid-like layer, liquid-like ice grain boundary, unfrozen solution, frozen aqueous solution, or micropocket. It can provide a unique environment for the chemical reactions and induce different reaction pathways from those in water.

The chemical reaction rate generally decreases with decreasing temperature according to the Arrhenius equation. However, some chemical reactions in the liquid region of ice (at relatively lower temperatures) proceed more rapidly than those in water (at relatively higher temperatures). The accelerated chemical reactions in ice can be classified into four categories: (1) reaction between solutes and dissolved gases (e.g., nitrite/oxygen (Takenaka et al., 1996; Takenaka et al., 1992), iodide/oxygen (Kim et al., 2016), and 1,1-diphenylethylene/ozone (Ray et al., 2011)), (2) reaction between solutes and water (e.g., fluorescein diacetate/water (Anzo et al., 2013)), (3) reaction between solutes and solutes (e.g., chromate/arsenite (Kim and Choi, 2011), chromate/hydrogen peroxide (Kim et al., 2015), and mercury/hydrogen peroxide (O'Concubhair et al., 2012)), and (4) dissolution of metal oxides (e.g., iron oxide (Jeong et al., 2012; Kim et al., 2010) and manganese oxide (Kim et al., 2012)). These reaction kinetics in ice are accelerated compared to those in water mostly due to the freeze concentration effect, that concentrates solutes, protons (at acidic conditions), and dissolved gases in the liquid region of ice and increases the thermodynamic driving force for chemical reactions (Finnegan et al., 2001; Takenaka and Bandow, 2007). The fate and behavior of chemical species (i.e., pollutants) in cold regions (e.g., permafrost, polar regions, and mid-latitudes during the winter season) can be notably different from those in warm regions due to the different chemical kinetics and mechanisms between water and ice.

Chromium (Cr) contamination in water occurs from both anthropogenic sources (e.g., discharge of industrial wastewater from corrosion inhibition, metallurgy, electroplating, leather tanning, and dye plants) and natural sources (e.g., weathering and dissolution of Cr-bearing minerals) (Barnhart, 1997; Vaiopoulou and Gikas, 2012). The World Health Organization (WHO) has established a provisional guidance value for Cr in drinking water (1 μM) (WHO, 2011). Cr exists mainly as metallic Cr (Cr^0), trivalent Cr (Cr(III)), and hexavalent Cr (chromate, Cr(VI)) in water. The toxicity of Cr species significantly depends on its oxidation state. Cr(VI) is more toxic than Cr^0 and Cr(III) due to its high transport capacity to the cell (Costa, 2003). Therefore, the European Union (EU) strictly restricts the concentration of Cr(VI) among various Cr species based on the European Restriction of Hazardous Substances Directive (EU, 2011).

Nitrite (NO_2^-) is one of the most abundant nitrogen species in the environment with nitrate (NO_3^-), ammonium (NH_4^+), and dinitrogen (N_2). Among these nitrogen species, NO_2^- is more toxic than the others to humans and animals (Abrol et al., 2007; Chen et al., 2011). Wastewaters from various industries, such as food preservation, corrosion inhibition, pharmaceutical, dye, and fertilizer, contain high concentrations of NO_2^- (Mackerness and Keevil, 1991; Walters, 1991). In addition, NO_2^- is produced from the biological reduction of NO_3^- by microorganisms under anoxic conditions (Cabello et al., 2004; Yan et al., 2016). It indirectly contributes to the eutrophication in surface waters and algal bloom in estuary waters as a source of nitrogen (Anderson et al., 2002). The reaction of NO_2^- with amino compounds in the human body forms *N*-nitroso compounds, which are highly toxic and carcinogenic (Cammack et al., 1999). NO_2^- can oxidize hemoglobin to methemoglobin, which reduces the oxygen transport ability in the blood and causes blue baby syndrome in infants (Jones et al., 2015). Therefore, the WHO recommends that the concentration of NO_2^- in drinking water should not exceed 4.3 μM (WHO, 2011).

Both Cr(VI) and NO_2^- are ubiquitous in various environments, such as atmospheric water, soil, surface water, groundwater, and

wastewater. Therefore, the coexistence of Cr(VI) and NO_2^- in the environment is fairly common. In this work, we compared the reduction of Cr(VI) by NO_2^- in ice (i.e., at -20°C) with that in water (i.e., at 25°C). The reduction of Cr(VI) by NO_2^- was significantly enhanced by freezing. The reduction of Cr(VI) to Cr(III) was accompanied by the oxidation of NO_2^- to NO_3^- . The reduction of Cr(VI) in ice was investigated as a function of various experimental parameters, such as NO_2^- concentration, pH, and freezing temperature. The reduction of Cr(VI) in real Cr(VI) -contaminated wastewater was also investigated to verify the environmental relevance of the freezing-enhanced reduction of Cr(VI) by NO_2^- . The mechanism of the enhanced Cr(VI) reduction by NO_2^- in ice and its environmental implications are discussed.

2. Chemicals and methods

2.1. Chemicals

The chemicals were used as received without further purification. They include sodium dichromate dihydrate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, Cr(VI) , Sigma-Aldrich, $\geq 99.5\%$), sodium nitrite (NaNO_2 , Sigma-Aldrich, $\geq 99.0\%$), sodium nitrate (NaNO_3 , Sigma-Aldrich, $\geq 99.0\%$), acetone (CH_3COCH_3 , Junsei, $\geq 99.5\%$), sulfuric acid (H_2SO_4 , Sigma-Aldrich, $\geq 95.0\%$), 1,5-diphenylcarbazine ($\text{C}_6\text{H}_5\text{NHNHCONHNHC}_6\text{H}_5$, DPC, Sigma-Aldrich, $\geq 99.95\%$), potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{K}_2\text{O}_4$, Junsei, $\geq 99.8\%$), sodium carbonate (Na_2CO_3 , Sigma-Aldrich, $\geq 99.5\%$), and sodium bicarbonate (NaHCO_3 , Sigma-Aldrich, $\geq 99.7\%$). Ultrapure deionized water (18.3 $\text{M}\Omega \cdot \text{cm}$) was used and prepared using a water purification system (Barnstead). The Cr(VI) -contaminated wastewater ($[\text{Cr(VI)}] = 106.2 \text{ mM}$ and $\text{pH} = 0.2$) was obtained from a local electroplating plant in Republic of Korea.

2.2. Experimental procedure

An aliquot of NO_2^- and Cr(VI) chemical stock solution was added to the deionized water in a beaker to yield the desired initial concentration (typically $[\text{Cr(VI)}] = 20 \mu\text{M}$ and $[\text{NO}_2^-] = 200 \mu\text{M}$). The pH of the solution was adjusted using HClO_4 (1 M) or NaOH (1 M) solution (typically $\text{pH} = 3.0$) and measured using a benchtop pH meter (Thermo Orion Star A211). First, 10 mL of this solution was put in a 15 mL conical tube. The conical tube was placed in a stainless steel tube rack in an ethanol bath adjusted to the desired temperature (typically -20°C) to freeze the aqueous sample. The time point when the conical tube was put into the ethanol bath was defined as reaction time zero in reaction kinetics measurements. The frozen samples were thawed in lukewarm water (35°C) and immediately analyzed. The experiments in water were identical to those in ice except for the temperature of ethanol bath. The aqueous samples were maintained at 25°C in the ethanol bath. All experiments were performed at least twice to confirm the data reproducibility.

2.3. Chemical analyses

The concentration of Cr(VI) was measured spectrophotometrically using the 1,5-diphenylcarbazine (DPC) method (Eaton et al., 1995). First, 100 μL of DPC reagent solution prepared with 0.05 g of DPC, 25 mL of acetone, and 250 μL of sulfuric acid was added to an amber vial containing 3 mL of aqueous sample. The aqueous solution was mixed vigorously and kept in the dark for 1 h. Then, its absorbance was measured at 540 nm using a UV-visible spectrophotometer (Shimadzu UV-2600).

The concentrations of NO_2^- and NO_3^- generated from the oxidation of NO_2^- were measured using an ion chromatograph (IC, Dionex ICS-1100) equipped with a Dionex IonPac AG14 guard column (4 mm \times 50 mm), a Dionex IonPac AS14 column (4 mm \times 250 mm), and a conductivity detector. The eluent consisted of a binary mixture

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